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APPLICATION OF HIGH FREQUENCY OSCILLATORS. RATES OF NEUTRALIZATION (NITRO-ACI CONVERSION) OF NITROPARAFFINS

by

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Technical Report No. 4

to the

OFFICE OF NAVAL RESEARCH

Under Project No. NR 051-318

Contract No. N6onr-23225

at the

Department of Chemistry

University of Michigan

Ann Arbor, Michigan

October 15, 1954

ABSTRACT

As part of the program for investigating the applicability of electrometric technics to the study of reaction kinetics, the one commercially available high frequency oscillator circuit, the Sargent Model V Oscillometer, has been used to follow the conversion by hydroxide ion of the normal form of nitroparaffins to the aci form. The compounds were studied in aqueous solution at 25° in millimolar concentration of sodium hydroxide and five- or ten-fold that concentration of nitroparaffin; the half-lives varied from 0.3 to 8.5 minutes, in which range the progress of the reaction could be followed by manual adjustment of the high frequency oscillator. The latter is a five-megacycle capacitive retune circuit.

The rates of neutralization of the six lower primary and secondary nitroparaffins studied decrease in the following order; nitromethane, nitroethane, 1-nitropropane, 1-nitrobutane, 2-nitropropane and 2-nitrobutane. The values of the second order reaction rate constants are in agreement with those found for the three lower nitroparaffins in nonbuffered solution at 0° and 5° by 1000-cycle conductivity measurements. Qualitatively, the present results are in agreement with those found for the four C_1 to C_3 nitroparaffins by polarographic measurement at 25° in buffered solution, although the ratio of pseudo first order rate constants differ.

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One of the objectives of ONR Project No. NR 051-318 is the investigation of the applicability of high frequency (megacycle range) oscillator circuits to the measurement of reaction rates. The general problem of the applicability of such experimental arrangements to reaction rate measurement was discussed in Technical Report No. 3 of the project, which report will be published in a forthcoming volume on the 1954 Faraday Society Discussion on rapid reaction rates (2). Studies involving one typical example of the necessary instrumentation and the measurement of the rates of hydrolysis of the lower aliphatic esters and of the esters of the three chloroacetic acids have been described in Technical Reports Nos. 11, 12 and 13 of the antecedent Project, NR 055-211, which studies have been published (3).

The general applicability of high frequency oscillators to organic chemistry was summarized in Technical Report No. 5 of Project No. NR 055-211, which was published as part of the report on a discussion of such oscillators (1). A consideration of the use of such oscillators in organic analysis is now in preparation. Current work on megacycle frequency oscillators is indicated in the quarterly Status Reports prepared on Project No. NR 051-318.

One of the specific aims in the objective cited at the beginning of this report is the possible utilization of commercially available megacycle frequency oscillators in rate measurement.

Investigation of such applicability is highly desirable if organic and physical chemists are to avail themselves of high frequency oscillator circuits. The need of constructing one's own equipment would undoubtedly serve as a deterrent for many people to the use of megacycle oscillators in at least some of the situations where such measuring devices could be of service. At present, the only commercially available suitable instrument is the Model V Oscillometer manufactured by E. H. Sargent and Co.; Beckman Instruments, Inc., apparently does not intend to put on the market at present the high frequency titrator which has been in development for a number of years. An Eastern apparatus company and supply house expects to put on the market in December, 1954, an oscillator which it has had in development.

The present report describes the application of the Sargent Model V Oscillometer to following the conversion of nitroparaffins to the aci form. The rates under the experimental conditions used were such that the course of reaction could be followed by manual operation of the measuring apparatus. It is unfortunate that a mechanical defect in the instrument caused the results to have less than the maximum precision possible; the final results, though, seem satisfactory.

The present work shows that investigations of certain types of ionic reactions whose half-lives are of the order of 20 seconds or longer can be carried out by means of the Sargent Model V Oscillometer without the use of recording devices.

In the present report certain items, e.g., the Oscillometer itself and the conversion of experimental measurements to kinetically useful data, have been treated in greater detail than they

would be in a paper submitted for journal publication. It is planned to abstract from this report a suitable scientific paper.

NEUTRALIZATION OF NITROPARAFFINS

The primary and secondary nitroparaffins have long been classified as pseudo acids on the basis of their relatively slow reaction in alkaline solution to form anions which are usually called the aci forms of the nitroparaffins:

$$R_1R_2CHNO_2 + OH^- = R_1R_2CNO_2^- + H_2O \qquad (1)$$

The reaction is generally considered as a neutralization; the mechanism of the reaction is discussed in references 5, 7 and 9. The rates of conversion of the normal to the aci forms have been investigated for the lower nitroparaffins under a variety of conditions.

Maron and Laller (5) used 1000-cycle frequency conductivity measurements to follow the neutralization at 0° and 5° C. of 0.003 to 0.040 N solutions of nitromethane, nitroethane and 2-nitropropane in water and in deuterium oxide to which an equivalent quantity of barium hydroxide or deuteroxide was added. The restriction to low temperatures was necessitated by the speed of the reaction at the concentrations employed. These investigators thoroughly reviewed previous work. Subsequently, Pearson (7) studied by a similar conductometric technique the rates of neutralization of nitroethane by ammonia and methylamines at 0° and 5°. Turnbull and Maron (9), using potentiometric measurements, determined the ionization constants of the normal and aci forms of nitromethane, nitroethane and 2-nitropropane. Miller, Arnold and Astle (6) studied polarographically the neutralization at 25° of

nitromethane, nitroethane, and 1- and 2-nitropropane by following the conversion of the reducible normal form to the polarographically non-reducible aci form; these workers used buffered solutions which were 1 millimolar in nitroparaffin.

It was, as previously indicated, the goal of the present investigation to attempt to extend the use of high frequency oscillators to the study of the kinetics of the neutralization of nitroparaffins by means of the one commercially available instrument, the Sargent Model V Oscillometer. Such an investigation is possible because of the large change in the conductivity of the solution as the reaction of equation (1) takes place, and hydroxide ion is replaced by the anion representing the aci form of the nitroparaffin. If we assume that equivalent conductances do not change over the range of ionic concentrations encountered in an experiment (as was assumed by Pearson and others for higher concentrations than those used in the present studies), the changes in the reaction represented by equation (1) can be written in terms of measured items which are linear functions of conductance.

Specifically, the present investigation covers reaction rate studies on the neutralization of six C_1 to C_4 nitroparaffins; the rates decrease in the following order: nitromethane, nitroethane, 1-nitropropane, 1-nitrobutane, 2-nitropropane and 2-nitrobutane. This is in accord with the findings of Miller, Arnold and Astle (6) who followed the similar reaction of the four lower nitroparaffins in buffered solutions. The data for nitroethane and 2-nitropropane is in good agreement with that of Maron and LaMer (5).

EXPERIMENTAL

Chemicals. The six nitro compounds studied had a mole purity of at least 99.9% as determined mass spectrometrically (see Table I), and were furnished by Dr. John A. Riddick of the Commercial Solvents Corporation. Solutions of 0.01 M nitroparaffin were prepared by weighing out the relatively volatile liquid from a modified medicine dropper. To minimize further any loss due to evaporation, the mouth of the volumetric flask was covered with a sheet of glassine powder paper which was perforated to admit the tip of the dropper. The flask was then filled to the mark with carbon dioxide-free distilled water, prepared by boiling distilled water for 10 minutes and allowing it to cool to room temperature in a capped bottle. The 0.01 M sodium hydroxide solution was prepared from a saturated sodium hydroxide solution which was diluted with carbon dioxide-free water to the desired concentration. The alkaline solution was then standardized against reagent grade potassium hydrogen phthalate and was stored in a polyethylene bottle.

Oscillator. The high frequency oscillator used in these experiments was the Sargent Model V Oscillometer which operates at a frequency of about 5 megacycles. Unfortunately, the specific instrument used had a certain instability in the power supply; the cause was not discovered until the work was completed; systematic drifts varying in direction of approximately 1 unit per minute were present. It is estimated that these drifts were responsible for a probable measurement error of about 3 per cent. The instrument is of the capacitive retune type, i.e., the sample cell is in parallel with calibrated condensers in the five-megacycle resonant circuit. A change in the sample composition produces

a change in the frequency of the circuit; the latter can be restored to the resonant frequency by adding or removing capacitance with the calibrated condensers.

Basically, the circuit consists of a series arrangement of a stable cathode coupled oscillator, an amplifier, a discriminator and a vacuum tube voltmeter (VTVM). The amplifier serves to isolate the oscillator, as well as to amplify and limit the input voltage to the discriminator. The discriminator is insensitive to amplitude changes of the signal voltage which it feeds to the VTVM circuit; the latter isolates the galvanometer from the discriminator. A regulated power supply is part of the instrument.

The capacitance-measuring array consists of a variable condenser and a series of fixed condensers, giving a range of thirty-two thousand scale units. The sensitivity of the instrument is about one scale unit which corresponds to a change of approximately 0.005 mmf.

The basis whereby such a capacitance-measuring instrument can be used to measure conductance, capacitance or a composite of both effects is indicated in reference 2.

The capacitance cells used were of the large size "titration" type furnished by the Sargent Company and had a capacity of about 160 ml. The cell is basically an annular space between two coaxial metallic cylinders which are sealed to glass cylinders; the dielectric in the space consists of the sample and of the two cylindrical glass walls between the plates and sample. Electrical connection between the cell plates and cell-holder is by means of spring contacts.

A detailed mechanical and electrical description of the instrument and its cells is given in a publication of the Sargent Company (2).

Constant Temperature Arrangement. The cell and cell-holder were maintained at a temperature of 25.0±0.2°C. by placing them in a constant temperature air bath (Figure 1). The bath was a hollow cylindrical vessel which was open at the top; a circular opening near the base permitted the insertion of the coaxial cable which connected the cell and cell-holder to the Oscillometer. The top of the air bath was covered with a circular disk of polystyrene foam; the opening around the coaxial cable was plugged with glass wool. Water from an external constant temperature bath, maintained at 25.0±0.1°C., was circulated through the air bath.

Apparatus Correction. It was noticed that when certain fixed condensers were removed from the measuring circuit in the course of taking readings that there was a sharp discontinuity in the plot of C_t, the instrument reading, vs. time. A corrective factor, estimated from this graph, was added to all readings which followed the break in the curve. This related all values to the same standard. Justification for such action can be found in the fact that all data collected in the region involving the same set of fixed condensers required approximately the same correction at the point of discontinuity. Very precise calibration was impossible because of an inherent drift in the instrument which resulted from the fault in the power supply previously mentioned.

Procedure. Before the actual samples were run, it was necessary to determine over what range of concentration the instrument reading was a linear function of concentration. Dilution experiments

indicated the latter to be true as long as the sodium hydroxide concentration did not exceed 0.001 M.

In an actual experiment, 100 ml of 0.001 M nitroparaffin solution was pipetted into a 125-ml. Erlenmeyer flask which was stoppered and suspended in the constant temperature bath (25.0±0.1°C.) for 15 minutes in order to reach temperature equilibrium. This solution was then mixed with 10 ml. of 0.01 M base. To insure adequate mixing, the resulting solution was poured twice between the vessels. A clock was started the instant the nitro compound and the base were mixed. The reacting solution was then transferred to a capacitance cell which was stoppered with a cork covered with aluminum foil, and which was placed in the cell-holder located in the air bath. Readings were taken at 15-second intervals until the reaction was complete; the first reading was usually taken within 30 seconds of mixing the reactants. For reactions which reached equilibrium slowly, readings were taken for the first ten minutes and then the solution was returned to the constant temperature bath where it was allowed to remain for several hours until equilibrium was reached. The equilibrium reading was then recorded.

DISCUSSION

Basis for the Calculations. If a large excess is taken of one of the reactants, e.g., the nitro compound, so that its concentration remains essentially constant, then the reaction which occurs can be considered as pseudo first order (see Equation (1)), and the following familiar expression applies:

$$\frac{dx}{dt} = - k' (a - x) \qquad (2)$$

where (a - x) is the concentration of the reacting species present

in smaller amount (original concentration = a) at any time t, and k' is the pseudo first order reaction rate constant.

Integrating equation (2) results in

$$\ln (a - x) = k' t + C \qquad (3)$$

If

$$(a - x) = K (C_t - C_a) \qquad (4)$$

where K is a proportionality constant, C_t is the instrument response to the conductance at any time, t, and C_a is the instrument response to the conductance at infinite time, then

$$C_t = K' [OH^-]_t + K'' [RNO_2^-]_t \qquad (5a)$$

and

$$C_a = K' [OH^-]_a + K'' [RNO_2^-]_a \qquad (5b)$$

where $[OH^-]_t$ and $[RNO_2^-]_t$ are the concentrations of hydroxide ion and of nitroparaffin anion at time t; K' and K'' are proportionality constants such that the instrument responses due to the conductances of hydroxide ion and nitroparaffin are K' $[OH^-]$ and K'' $[RNO_2^-]$, respectively; etc. Therefore,

$$C_t - C_a = K' ([OH^-]_t - [OH^-]_a) + K'' ([RNO_2^-]_t - [RNO_2^-]_a) \qquad (6)$$

Since

$$[RNO_2^-]_t = a - [OH^-]_t \qquad (7)$$

where "a" is the initial $[OH^-]$, equation (6) can be changed to

$$C_t - C_a = (K' - K'') ([OH^-]_t - [OH^-]_a) \qquad (8)$$

Equation (8) indicates that if the assumptions made are valid, $(C_t - C_a)$ is a function only of the concentrations of the hydroxide ion at time t and at infinite time. If we work in the range where the instrument response is a linear function of the concentration, then $(C_t - C_a)$ is linearly related to the change in concentration of the hydroxide ion at those respective times.

From equations(3) and (4), it follows that

$$\ln K (C_t - C_a) = -k' t + C \qquad (9)$$

and

$$\log (C_t - C_a) = - (k'/2.3)t + C' \qquad (10)$$

Consequently, a plot of log $(C_t - C_a)$ against t should give a straight line whose slope is equal to $- k'/2.3$. If $k'/2.3$ is multiplied by (2.3/concentration of the substance in excess), the second order reaction rate constant can be obtained.

The general derivation of equations for the correlation of physical properties with concentration, of which the foregoing is a specific example, is considered by Frost and Pearson (4).

Treatment of Data. Data for a typical run are given in Table II. When $(C_t - C_a)$ is plotted on the logarithmic ordinate of a semilog graph against time, a curve of the type shown in Figure 2 is obtained. The slope of this line, -0.933, can be used to calculate the pseudo first order reaction rate constant by equation (10):

$$-0.933 \text{ min}^{-1} = - k' /2.3 \qquad (11)$$

The half-life can then be obtained from the expression for a first order reaction

$$t_{1/2} = \frac{\ln 2}{k'} \qquad (12)$$

as 0.323 min. The second order reaction rate constant, k, is related to the pseudo first order constant by

$$k' = k \text{ (concn. of species in excess)} \qquad (13)$$

The species in excess in this case is the nitroethane; hence,

$$k = 2.303 \times \frac{k'}{2.303} \times \frac{1}{0.009193} = 235 \text{ l. moles}^{-1} \text{ min}^{-1} \qquad (14)$$

Kinetic Data. A summary of the data for the six nitroparaffins studied, including pseudo first order rate constants, calculated second order rate constants, and half-lives, is given in Table III. The average deviations of the means of the second order rate constants range from 0.6 to 4.9% with only one average deviation exceeding 2.1%.

Effect of Possible Reverse Reaction. The present mathematical treatment which is essentially based on a simple first order reaction and does not make explicit allowance for the effect of opposing reactions, is strictly valid only for reactions where the equilibrium point of the reaction of equation (1) lies so far to the right that secondary effects become negligible. With this in mind, the slopes of the curves have been calculated from the initial values so as to overcome as much as possible the influence of the reverse reaction.

However, it is well known (p. 173 of reference 4) that when the equilibrium concentration is explicitly introduced in the calculations, a first order expression is observed for a reversible reaction with the effective rate constant being the sum of the constants for the forward and reverse directions.

It is possible to estimate, at least qualitatively, the effect of the reverse reaction on the specific reactions studied.

Miller, Arnold and Astle (6), using polarographic measurements, found the ratios of the nitro to the aci forms at equilibrium at pH 8.9 to be 0.71, 0.20, 0.42, and 0.78 for nitromethane, nitroethane, 1-nitropropane and 2-nitropropane, respectively. At this pH, our reactions should theoretically have gone 99% to completion. In

the present calculations on nitromethane, where the half-life is of the order of 20 seconds and the equilibrium point is apparently unfavorable, it is possible that the reverse reaction played an important part. The unfavorable influence of reverse reactions on the rates of nitroethane and 1-nitropropane, which are almost as rapid as the nitromethane, is off-set, at least in part, by their more favorable equilibrium points. Because of the lack of data, we can only surmise that the same holds true for the 1-nitrobutane as for the nitroethane and the 1-nitropropane. The consequences of the unfavorable equilibrium point of 2-nitropropane are considerably reduced by the fact that the calculations are based upon the first 2 to 3 minutes of the reaction; the half-life of this process is about 4.5 minutes, and, hence, secondary effects are probably small. Even though no data are available on the equilibrium point of 2-nitrobutane, the same argument probably holds since the half-life of this reaction is approximately 8.5 minutes, and once again the calculations were based on the first 2 to 3 minutes of the reaction. The values for the equilibrium ratios of nitro to aci forms given by Miller, Arnold and Astle may be higher than they should be[1]; if this were so, the effects of the reverse reactions would be even less than discussed in this paragraph.

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[1]There is a possible source of error in the polarographic measurements on the nitroparaffin-aci form equilibrium due to the regeneration of the normal form from the aci form at the electrode-solution interface during the life-time of the mercury drop as the normal form is removed by reduction. This effect has been observed with other acid-anion systems, e.g., Brdicka and Wiesner, Collection Czechoslov. Chem. Communs. 12, 138 (1947).

Evaluation of the Results. Qualitatively, the results are in agreement with those of Miller, Arnold and Astle (6), for the four compounds which they studied. The other two compounds studied in the present investigation seem to fall into their logical places; the rates decrease in the following order: nitromethane; nitroethane, 1-nitropropane, 1-nitrobutane, 2-nitropropane and 2-nitrobutane.

Since Miller, Arnold and Astle carried out their reactions at considerably higher ionic strength and in buffered solution at constant pH, it is not surprising that the present data does not agree quantitatively with theirs. For example, at 25°C., for 2-nitropropane, 1-nitropropane, nitroethane and nitromethane, they find for the pseudo first order rate constants, taking that of 2-nitropropane (0.0081 $min.^{-1}$) as unity, the ratio of 1.00: 1.73: 2.72: 2.22 in a buffered solution of pH 8.9 as compared to a ratio of 1.00: 10.5: 12.7: 14.7 found in the present study (extension of the latter ratio to the 1-nitrobutane and 2-nitrobutane measured in the present study is 10.2: 0.483; k' for 2-nitropropane = 0.0295 $min.^{-1}$). Duplication of their work was not feasible since the high ionic strength required for the maintenance of a buffered solution was not permissible with our measuring device. Attempts to run the reactions at lower concentrations but within the boundaries imposed by the conductivity of the solution, were not successful; the rates were so slow that their determination was not practical.

A more pertinent comparison for the present results would be with those of Maron and LaMer (5), who also worked in unbuffered solution. Their ratio of the second order rate constants for 2-nitropropane, nitroethane and nitromethane at 0°C. is 1.0: 18: 114 as compared to the ratio found in the present study at 25°C.

of 1.0: 14: 63. Maron and Lalier give values of the second order rate constant at 0° and 5° for 2-nitropropane and nitroethane; calculation of the rate constants at 25° by the Arrhenius equation gives values of 19.4 and 253. In view of the uncertainty in the activation energy value based on a difference of 5°, these values are in good accord with those found at 25° in the present study, i.e., 16.4 and 236.

The precision of the results obtained in the present study indicate that the Sargent Model V Oscillometer can be used advantageously for studying the kinetics of moderately rapid reactions in solutions of low ionic strength that are not hindered by unfavorable equilibria.

In future work, it would be desirable to attempt to apply the Oscillometer to (a) a nonaqueous system where capacitance changes rather than conductance changes were being measured, and (b) a sufficiently rapid reaction that the data would have to be recorded on a recording potentiometer or an oscillograph.

ACKNOWLEDGMENT

The authors would like to thank the Office of Naval Research which supports the project, of which the work herein described is a part. They also want to express their gratitude to E. H. Sargent and Company for the loan of the Model V Oscillometer and to Dr. John A. Riddick of the Commercial Solvents Corporation who supplied the nitroparaffin samples studied.

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Table I. Purity of the Nitroparaffins Used As Determined by Mass Spectrometry[a]

Compound	Impurities present, mole-%[b]					
	CH_3NO_2	$C_2H_5NO_2$	$1\text{-}C_3H_7NO_2$	$2\text{-}C_3H_7NO_2$	$1\text{-}C_4H_9NO_2$	$2\text{-}C_4H_9NO_2$
CH_3NO_2	100.0	0.00	.....	-0.05	.....	0.00 .....
$C_2H_5NO_2$	0.04	99.7	.....	0.24	.....	0.01 .....
$1\text{-}C_3H_7NO_2$	0.01	0.01	99.98	0.00	.....	0.00 .....
$2\text{-}C_3H_7NO_2$	0.00	-0.04	0.00	100.0	.....	0.00 .....
$1\text{-}C_4H_9NO_2$	0.00	0.00	.....	0.16	100.00	-
$2\text{-}C_4H_9NO_2$	0.00	-0.21	.....	-0.04	-	100.0

[a]Data furnished by Dr. Riddick of the Commercial Solvents Corp., who furnished the samples.

[b]Negative values are due to the fact that the samples are purer than the standards used in calibrating the mass spectra.

Table II. Neutralization of Nitroethane: Data for a Typical Experiment

Time, min.	Oscillometer Units (C_t)	$C_t - C_a$
0.50	24,727	688
0.75	415	376
1.00	254	215
1.25	167	128
1.50	117	78
1.75	085	46
2.00	067	28
2.25	055	16
2.50	052	13
2.75	049	10
3.00	044	-
3.25	040	-
3.50	-	-
3.75	-	-
4.00	039	-

Table III. Rate Data for the Conversion of Nitroalkanes to the Aci Form

Compound and concn.	NaOH concn.	$k'/2.303$	$t_{1/2}$	Second order rate constant, k
mM	mM	$min.^{-1}$	min.	$l.\ mole^{-1}\ min^{-1}$
nitromethane				
2.419	0.514	1.08	0.279	1032
		1.07	0.281	1020
				Av. 1026 ± 6 (0.6%)
nitroethane				
9.143	0.919	0.972	0.310	244
		0.910	0.331	229
		0.933	0.323	235
				Av. 236 ± 5 (2.1%)
1-nitropropane				
9.199	0.999	0.769	0.391	193
		0.774	0.389	194
		0.787	0.382	197
				Av. 195 ± 2 (1.0%)
2-nitropropane				
9.573	0.999	0.0638	4.72	15.4
		0.0656	4.59	15.8
		0.0667	4.51	16.0
		0.0713	4.22	17.2
		0.0727	4.14	17.5
				Av. 16.4 ± 0.8 (4.9%)
1-nitrobutane				
9.105	0.999	0.787	0.382	199
		0.726	0.415	184
		0.757	0.397	191
		0.763	0.394	193
				Av. 192 ± 4 (2.1%)
2-nitrobutane				
9.309	0.999	0.0354	8.50	8.75
		0.0356	8.50	8.82
		0.0347	8.67	8.58
		0.0365	8.24	9.02
		0.0352	8.55	8.71
				Av. 8.78 ± 0.12 (1.4%)

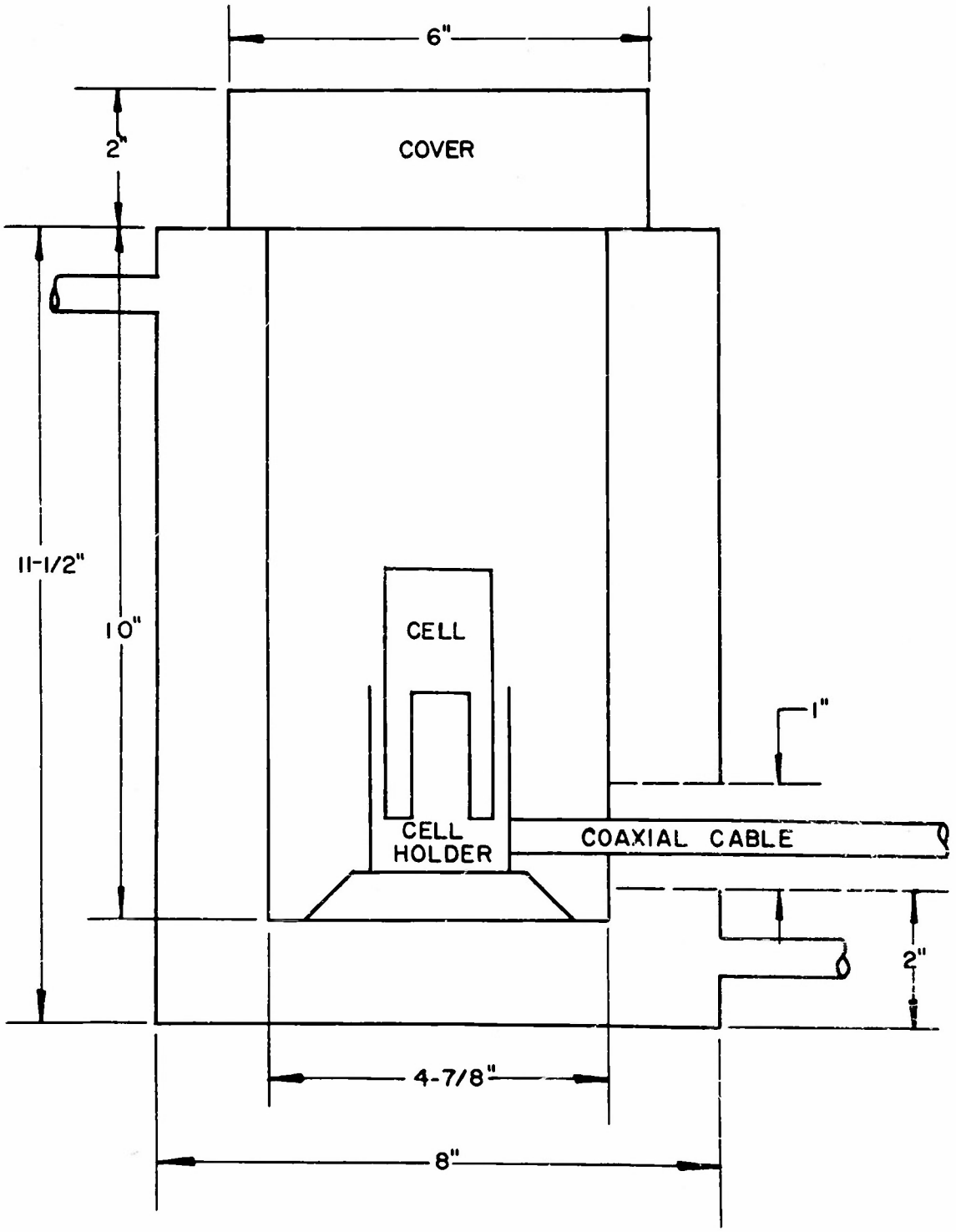

FIG. I. AIR BATH FOR THERMOSTATING MEASURING CELL AND HOLDER

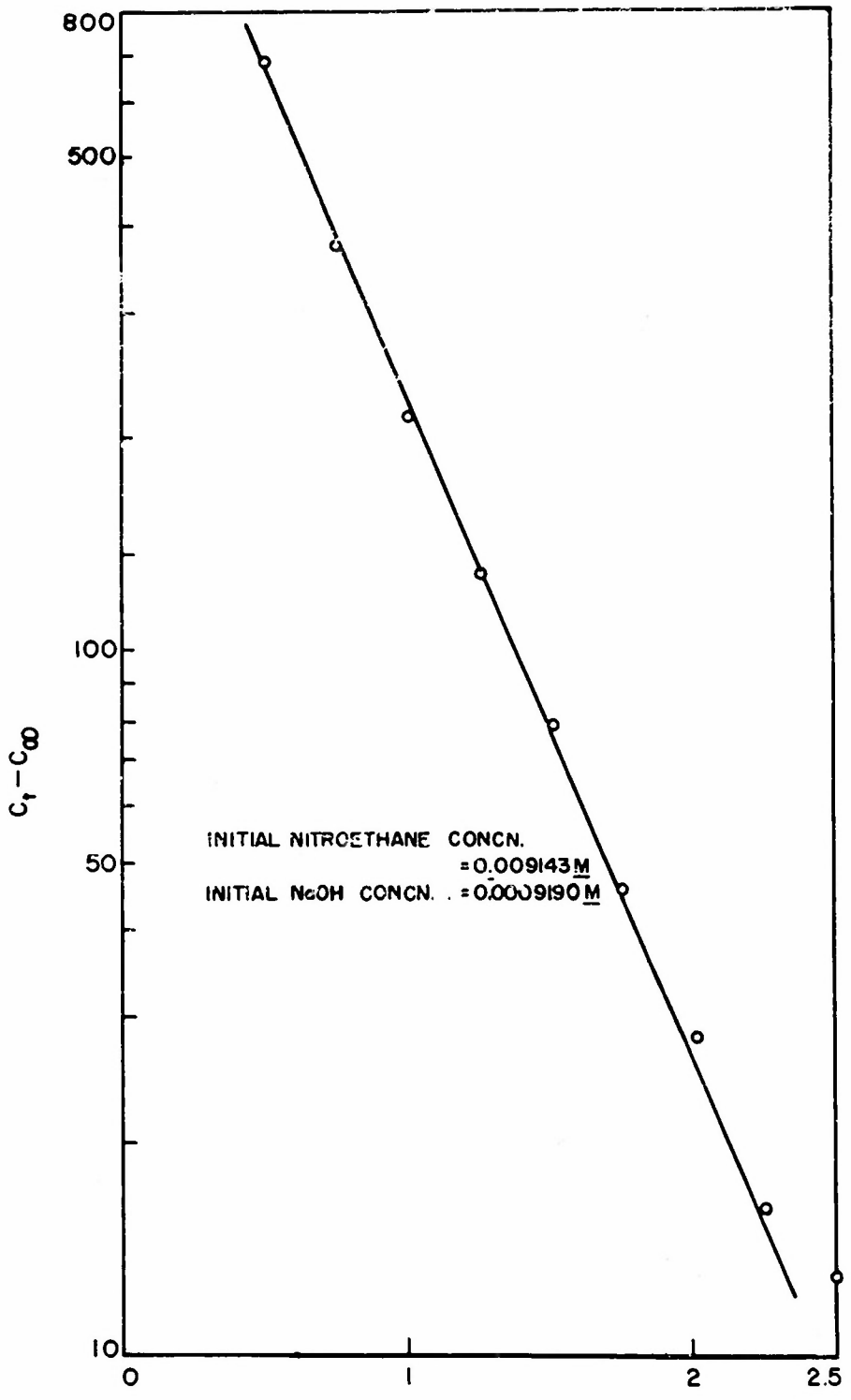

FIG.2. RATE OF NEUTRALIZATION OF NITROETHANE